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National Aeronautics
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EFFECT OF NITRIC OXIDE ON PHOTOCHEMICAL OZONE FORMATION IN MIXTURES OF AIR WITH MOLECULAR CHLORINE AND WITH TRICHLOROFLUOROMETHANE

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SUMMARY

An experimental and theoretical study was made of ozone (O_3) formation in air containing either molecular chlorine (Cl_2) and nitric oxide (NO) or trichlorofluoromethane ($CFCl_3$) and NO. The purpose of this work was to study the NO_x and ClO_x mechanisms for O_3 destruction. Similar mechanisms have been proposed for O_3 destruction in the stratosphere by NO and $CFCl_3$. Mixtures of these gases in air were photolyzed at room temperature and atmospheric pressure by ultraviolet, simulated solar radiation. Concentration-against-time profiles of O_3, NO, and NO_2 were measured. A temporary rise in O_3 concentration was observed for both Cl_2-NO-air and $CFCl_3$-NO-air mixtures. Ozone concentration then decreased and, in the case of $CFCl_3$-NO-air, stayed close to zero during the entire 3- to 4-hour reaction. A chemical mechanism that satisfactorily explains the experimental results was developed with the aid of a general chemical kinetics computer code. Computations show that the experimental O_3 concentration behavior is explained by the formation and subsequent destruction of chlorine nitrate ($ClONO_2$).

The gas-phase part of the chemical mechanism was used to compute O_3 formation in $CFCl_3$-NO-air mixtures at stratospheric temperatures, pressures, and compositions. There was a large reduction in the steady-state O_3 concentrations for these mixtures as compared with pure air. These computations did not use a complete stratospheric model, since transport phenomena were not included. They were performed to show the effect of the laboratory-derived chemical mechanism when it is applied at stratospheric conditions. The computations indicate that $ClONO_2$ will probably not be a major factor in preventing O_3 destruction in the stratosphere.

INTRODUCTION

Two previous reports (refs. 1 and 2) describe the effect of various pollutants on ozone (O_3) formation when air is photolyzed in a laboratory experiment. This work was done to obtain a better understanding of the chemistry of O_3 destruction. Chemical mechanisms involved in stratospheric O_3 destruction by these pollutants are similar to those in the laboratory simulations. The species studied were nitric oxide (NO) and one of the chlorofluoromethanes, trichlorofluoromethane ($CFCl_3$). The controversy over the extent of stratospheric O_3 depletion by these pollutants is well known (refs. 3 to 7). In reference 2, we showed that NO had only a temporary effect in delaying O_3 formation when air was photolyzed by simulated solar radiation in a static reaction chamber. Although 1 to 2 ppm of NO delayed O_3 formation at first, the O_3 concentration rose after a short delay (20 to 100 min) to the value it would have attained for pure-air photolysis. On the other hand, 1 to 100 ppm of $CFCl_3$ had a permanent destructive effect on O_3 formation in a similar experiment (ref. 1). The O_3 concentration either leveled off at a value lower than that for pure air or went through a maximum and decreased toward zero.

Recently, there has been discussion about the interaction of the NO_x and ClO_x destruction mechanisms for O_3 (ref. 8). By reacting with each other, the NO_x and ClO_x species may be partly removed, thus lessening the O_3 destruction. Therefore, we extended our previous work to the photolysis of mixtures of NO and $CFCl_3$ in air. In order to study a simpler but very similar chemical system, we also photolyzed mixtures of Cl_2 and NO in air.

Ozone formation was measured in Cl_2-NO-air and $CFCl_3$-NO-air mixtures in a static reaction chamber. The mixtures were irradiated with ultraviolet simulated solar radiation to find out whether the two O_3 destruction mechanisms reinforce each other or interfere with each other. Concentration profiles of NO and NO_2 were also measured. All experiments were performed at atmospheric pressure and room temperature (298 K). A chemical mechanism to help in understanding the experimental results was developed by performing theoretical computations. These kinetic computations, which attempted to match the observed O_3, NO, and NO_2 concentration profiles, were performed with an improved version of the general kinetics computer code of Bittker and Scullin (ref. 9).

The chemistry of NO_x and ClO_x systems has been studied for many years. The NO_x cycle for O_3 destruction is shown in the following set of reactions[1]:

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[1]Numbering of reactions corresponds to the complete list in table I.

$$NO + O_3 \xrightarrow{k_{14}} NO_2 + O_2 \qquad \text{(XIV)}$$

$$O + NO_2 \xrightarrow{k_{15}} NO + O_2 \qquad \text{(XV)}$$

$$NO_2 + O_3 \xrightarrow{k_{16}} NO_3 + O_2 \qquad \text{(XVI)}$$

$$NO_2 + h\nu \xrightarrow{J_{17}} NO + O \qquad \text{(XVII)}$$

The net result of reactions (XIV) and (XV) is the destruction of odd oxygen, $O + O_3 \rightarrow 2\ O_2$. When a chlorofluoromethane such as $CFCl_3$ is subjected to ultraviolet radiation, it dissociates into Cl atoms. The resulting Cl atoms start the ClO_x cycle for odd oxygen destruction:

$$Cl + O_3 \xrightarrow{k_1} ClO + O_2 \qquad \text{(I)}$$

$$O + ClO \xrightarrow{k_2} Cl + O_2 \qquad \text{(II)}$$

$$ClO + h\nu \xrightarrow{J_5} Cl + O \qquad \text{(V)}$$

The net result of reactions (I) and (II) is also $O + O_3 \rightarrow 2\ O_2$. When both chlorine compounds and NO are present in a reacting system, the following reaction can occur:

$$NO + ClO \xrightarrow{k_{21}} Cl + NO_2 \qquad \text{(XXI)}$$

Although this reaction ties up NO, it also produces Cl. So it is not obvious whether it will interfere with or aid in the O_3 depletion process. In addition, the formation of chlorine nitrate ($ClONO_2$) by the recombination of ClO and NO_2 has been well established (refs. 10 and 11).

$$ClO + NO_2 + M \xrightarrow{k_{22}} ClONO_2 + M \qquad \text{(XXII)}$$

If $ClONO_2$ is very stable, O_3 destruction would be decreased by the tieing up of ClO and NO_2. However, $ClONO_2$ is readily photolyzed by ultraviolet radiation, either in the laboratory or in the stratosphere, as follows (ref. 12):

$$ClONO_2 + h\nu \xrightarrow{k_{23}} ClO + NO_2 \qquad \text{(XXIII)}$$

Computations by Eggleton, Cox, and Derwent (ref. 13) indicate that $ClONO_2$ has a quite high concentration in the stratosphere and thus that it might be a significant sink for Cl atoms. However, later computations by Rowland, Spencer and Molina (ref. 11) show much smaller $ClONO_2$ stratospheric concentrations. Obviously, the results of such computations depend partly on having an accurate chemical reaction mechanism.

In this experiment, we studied the chemical system used for the stratospheric work, but at nonstratospheric conditions. The pressure and temperature are higher and there are walls, which can affect the reaction kinetics.

The chemical mechanism that was developed to explain the laboratory results was then used in a computation at stratospheric conditions by eliminating the wall reactions. This latter computation does not use a complete stratospheric model since radiative heat transfer and mass transport are not included, just as they were not included in the reaction chamber computations. It indicates the expected results of a static gas-phase reaction at altitude conditions. The same chemical mechanism could show quite different trends in species formation for widely different conditions of temperature, pressure, and initial composition. It is therefore important to determine whether our mechanism predicts the same effect on O_3 formation at low temperature and pressure that was observed and computed at reaction chamber conditions. The results of computations to check on this point are presented.

APPARATUS AND PROCEDURE

The reaction chamber used for this work was used in our previous work (refs. 1 and 2). It is a 650-liter stainless steel tank with about 85 percent of the inner walls lined with Teflon sheets. This surface reduces heterogeneous reactions involving O_3 and other free radicals. Ultraviolet simulated solar radiation with wavelengths as low as 200 nanometers was obtained from a high-pressure xenon arc lamp. Commercially available gases were used as sources of NO and "ultrapure" air. The Cl_2 and $CFCl_3$ were distilled twice in the laboratory before use. The "ultrapure" air contained less than 0.1 part per million (ppm) of methane and 1 to 2 ppm of water.

We measured profiles of O_3, NO, and NO_2 concentrations as a function of time when various mixtures of the pollutants in air were irradiated in the reaction chamber.

All experiments were performed at room temperature (298 K) and atmospheric pressure.

In this work six different types of mixtures were irradiated:

(1) Pure air

(2) Air + Cl_2

(3) Air + $CFCl_3$

(4) Air + NO

(5) Air + Cl_2 + NO

(6) Air + $CFCl_3$ + NO

The experiments were divided into two series. Series A involves Cl_2, NO, and air; series B involves $CFCl_3$, NO, and air. The two series of experiments were performed several months apart, but each series was run over a period of about 3 weeks. During the series A experiments, runs were made with Cl_2-air, NO-air, and Cl_2-NO-air mixtures. In addition, runs with pure air were performed at the beginning and end of the complete series. This procedure gave a self-consistent set of results for comparison purposes. The pure-air runs also "calibrated" the chamber and helped insure that chamber characteristics such as surface activity and light source intensity did not change significantly over the time interval for the complete series A. For these same reasons, the series B experiments included runs with pure air, $CFCl_3$ + air, NO + air, and $CFCl_3$ + NO + air.

EXPERIMENTAL RESULTS

Cl_2-NO-Air System

Two different mixtures of Cl_2 and NO in air were irradiated in the reaction chamber. Mixture 1 contained 2-ppm Cl_2 and 2-ppm NO, while mixture 2 contained 4-ppm Cl_2 and 2-ppm NO. Two mixtures of Cl_2 with air and a mixture of NO with air were photolyzed very close to the time of the NO-Cl_2 experiments in order to obtain data to use as a reference. As in our previous work, pure air was photolyzed before and after this complete series of experiments in order to obtain reference O_3 formation profiles.

Figure 1 shows measured profiles of O_3, NO, and NO_2 concentrations as a function of time for the two Cl_2-NO-air mixtures. For mixture 1 (fig. 1(a)), O_3 was formed more slowly than in pure air, but then the O_3 concentration rose steadily. The O_3 concentration leveled off after about 240 minutes of reaction. The O_3 profile is significantly different for mixture 2 (fig. 1(b)). After the same delay noted for mixture 1, the O_3 concentration rose to a maximum value of 25 parts per hundred million (pphm) at 70 minutes and then decreased. There is a hint of this effect in figure 1 also. It reached a minimum and then increased steadily after that. Both mixtures show similar

trends in the NO and NO_2 concentration profiles. The NO was rapidly consumed and NO_2 was formed. For both mixtures the NO_2 concentration reached a maximum and then decreased. However, the rate of decrease was much faster for mixture 2 than for mixture 1, which had the smaller amount of Cl_2 present at the start. These profiles are compared in more detail later in this section.

Figure 2 shows a comparison of O_3 concentration profiles for pure air, air + Cl_2, air + NO, and air + Cl_2 + NO. In figure 2(a), initial concentrations of Cl_2 and NO are each 2 ppm. The NO-air mixture showed the longest O_3 formation delay, as compared with pure air. The slightly shorter delay until the first detection of O_3 for the NO-Cl_2-air mixture (mixture 1) indicates that NO destruction of O_3 was counteracted slightly by the combined mixture. For all pollutant mixtures the destruction of O_3 was only temporary. In figure 2(b), initial concentrations of Cl_2 and NO are 4 ppm and 2 ppm, respectively. In this case the Cl_2-air mixture showed an O_3 formation delay longer than that of the NO-air mixture. However after 130 minutes, the two O_3 curves almost coincide. The O_3 formation curve for the NO-Cl_2-air mixture (mixture 2) shows the temporary early rise already noted. However, the effective delay for this mixture was much longer than for either pollutant separately. Mixture 2 temporarily impeded O_3 destruction but then the NO_x and ClO_x mechanisms reinforced each other. The reason for the temporary rise in O_3 concentration is discussed in the section DISCUSSION AND CONCLUDING REMARKS.

The effect of added Cl_2 on the NO and NO_2 profiles is shown in figure 3. Increasing Cl_2 concentration from 0 to 4 ppm steadily accelerated the consumption of NO, as shown in figure 3(a). Figure 3(b) shows that this Cl_2 addition not only accelerated NO_2 formation, but also accelerated its destruction after its concentration reached a maximum. This was probably due to the increasing importance of reactions XXI and XXII as Cl_2 concentration increased

$CFCl_3$-NO-Air System

One mixture of $CFCl_3$ with NO in air was photolyzed in this work. The concentration of O_3 as a function of time for 12-ppm $CFCl_3$ plus 1.5-ppm NO in air is shown in figure 4. Trichlorofluoromethane is much more difficult to photolyze than Cl_2. Therefore, a relatively large amount had to be used so that a strong effect on O_3 formation would be observed in a practical laboratory time. Also shown in figure 4 are a pure-air reference curve, a curve for 16-ppm $CFCl_3$ in air, and one for 1.3-ppm NO in air. The latter curves were obtained at the same time as the one for the NO-$CFCl_3$ mixture.

For $CFCl_3$ alone, the O_3 concentration rose immediately but soon reached a maximum and then decreased toward zero. This behavior is also reported in reference 1.

The effect of $CFCl_3$ on O_3 formation was slower than the effect of Cl_2 because $CFCl_3$ photolyzes much more slowly than Cl_2. Once O_3 destruction began, the effect of $CFCl_3$ was more permanent than the effect of Cl_2. The reason is that all the Cl_2 was rapidly photolyzed, while only a small fraction of the $CFCl_3$ was photolyzed during the total reaction time. The NO-air mixture delayed O_3 formation for about 120 minutes, but it then rose slowly and steadily. This delay is slightly longer than the 100-minute delay reported in reference 2 for a similar NO-air mixture. When the NO-$CFCl_3$ mixture was photolyzed, O_3 formation was delayed about 60 minutes. The O_3 concentration then rose but reached a maximum and then decreased sharply toward zero. Again, the interaction of the NO_x and ClO_x mechanisms to reduce O_3 destruction was only temporary.

Concentrations of NO and NO_2 as a function of time for the $CFCl_3$-NO-air mixture are presented in figure 5. They show the typical rapid conversion of NO to NO_2 and the subsequent loss of NO_2 that was observed previously (ref. 2).

COMPARISON OF EXPERIMENTAL AND THEORETICAL RESULTS

As in our previous work, chemical modeling computations were performed in order to explain the experimental results and to get a better understanding of the complex chemical mechanism involved.

Cl_2-NO-Air System

The NO_x chemical reaction mechanism of reference 2 was combined with the ClO_x mechanism of reference 1 to give the main part of the chemical model used for these computations. In addition, the reactions involving NO_x and ClO_x interactions (reactions XXI to XXIII) were added. Two other reactions of $ClONO_2$ are also included:

$$O + ClONO_2 \xrightarrow{k_{24}} ClO + NO_3 \qquad \text{(XXIV)}$$

$$Cl + ClONO_2 \xrightarrow{k_{25}} Cl_2 + NO_3 \qquad \text{(XXV)}$$

The complete list of reactions used and their rate constants are given in table I. The rate constant for O_2 photolysis

$$O_2 + h\nu \xrightarrow{J_7} O + O \qquad \text{(VII)}$$

was determined for each series of experiments. This was done by performing computations to match the experimental O_3-against-time profiles for pure air, which were taken before and after each series of experiments. The initial slope of this reference O_3 profile was determined primarily by J_7. The value $J_7 = 2.5 \times 10^{-9}$ sec^{-1} was used for these Cl_2-NO computations. This value corresponds to the pure-air O_3 curve of figure 2.

Two simulated wall destruction reactions are also needed to explain the results, as in our previous work (refs. 1 and 2). These are wall destruction of O_3 and Cl and are written

$$O_3 \xrightarrow{k_D} (3/2)O_2$$

$$Cl \xrightarrow{k_{Cl}} \frac{1}{2}N_2$$

The latter unbalanced reaction does not affect the mass balance of the system because the Cl concentration is always small and the ratio of N_2 concentration to Cl concentration is quite high. An approximate value of k_D was obtained by matching the pure-air reference curve. However, k_D was adjusted slightly to match the O_3 curves in the presence of pollutants. The value $k_D = 8 \times 10^{-4}$ sec^{-1} was used for these Cl_2-NO-air computations. The justification for invoking Cl wall destruction is discussed fully in reference 1. A constant value of k_{Cl} was used in that work in the presence of a few ppm of Cl_2. The value $k_{Cl} = 3.5$ sec^{-1} used in the present computations is about one-tenth of the value used for Cl_2-air mixtures in reference 1. This difference is due to small changes in wall surface characteristics and relatively high sensitivity of Cl wall destruction reactions to wall conditions.

A comparison of computed and experimental O_3 profiles for two mixtures of Cl_2 and NO is shown in figure 6. Each computed curve is the best of several trials in which a few of the reaction rate constants were varied within their experimental uncertainties. The largest variation was by a factor of 2. The curves were chosen by the authors on the basis of the general shape of the curve as well as the closeness of fit. There is semi-quantitative agreement between the experimental and computed curves for both mixtures. For 4-ppm Cl_2 (mixture 2) the computation reproduced the O_3 concentration maximum rather well and gave fair agreement with the rest of the experimental curve (fig. 6(b)). For 2-ppm Cl_2 (mixture 1) the computed O_3 curve still shows a maximum at about 65 minutes, but the experimental curve shows only a slight bending over at this point (fig. 6(a)). However, after the computed concentration begins to rise again, it follows the experimental curve fairly well. Concentration profile comparisons for NO

and NO_2 with these same two mixtures are shown in figure 7. Again, the computed curves are in fairly good agreement with experiment, except for the NO_2 profile of mixture 1. The computed curve decreases from its maximum much faster than the experimental curve.

These computations involved all the reactions and rate constants in table I, along with the simulated wall destruction reactions previously mentioned. The computations were repeated without the $ClONO_2$ reactions. The results did not reproduce the shapes of the experimental curves and are not shown. Thus, the $ClONO_2$ reactions are needed to explain the experimental results.

$CFCl_3$-NO-Air System

In addition to the reactions already used, the following reactions (refs. 14 and 15) have been added for the photolysis of $CFCl_3$:

$$CFCl_3 + h\nu \xrightarrow{J_{26}} CCl_2F + Cl \qquad \text{(XXVI)}$$

$$CCl_2F + O_3 \xrightarrow{k_{27}} CFCl_2O + O_2 \qquad \text{(XXVII)}$$

$$CFCl_2O \xrightarrow{k_{28}} CFOCl + Cl \qquad \text{(XXVIII)}$$

$$CCl_2F + O_2 \xrightarrow{k_{29}} CFCl_2O_2 \qquad \text{(XXIX)}$$

The photolytic formation of Cl atoms is the most important of these reactions. Because the decomposition of $CFCl_3$ is quite complicated, this mechanism is probably not complete. It is, however, the best available at this time. The rate constants used for these reactions are those used in reference 1. The values are $J_{26} = 1.3\times10^{-6}$, $k_{27} = 5\times10^{12}$ cm^3/mole sec, $k_{28} = 1\times10^{-2}$ sec^{-1}, and $k_{29} = 1\times10^{8}$ cm^3/mole sec. The values of k_{27}, k_{28}, and k_{29} were estimated because no experimental values for these rate constants have been reported in the literature. As shown in reference 1, the computed results are quite insensitive to the values of these last three rate constants. The value $J_7 = 1.2\times10^{-9}$ sec^{-1} was used for the O_2 photolysis. This value corresponds to the pure-air O_3 curve shown in figure 4. The values $k_D = 7.5\times10^{-4}$ sec^{-1} and $k_{Cl} = 0.1$ sec^{-1} were used for the O_3 and Cl wall destruction reactions in these $CFCl_3$-NO computations. Again, the value of k_{Cl} is about one-tenth of the value used for the $CFCl_3$ computations in reference 1.

Figure 8 shows experimental and computed O_3-against-time profiles for a mixture of 12-ppm $CFCl_3$ and 1.5-ppm NO. The overall agreement is good, with a very good reproduction of the observed maximum in O_3 concentration. Concentration profiles for NO and NO_2 are shown in figure 9 for this $CFCl_3$-NO mixture. The agreement between computed and observed profiles is quite good for both species. Our computations have been able to reproduce all measured profiles for this one $CFCl_3$-NO mixture.

Application to Stratospheric Conditions

This work has shown that $CFCl_3$ and NO together permanently inhibit O_3 formation in laboratory experiments. However, these conditions are much different from stratospheric temperatures, pressures, and concentrations. As in our previous work, we wanted to determine the effect on O_3 formation shown by our mechanism at stratospheric conditions, assuming that the same gas-phase chemical model applies. Therefore, we computed O_3 formation time profiles and steady-state concentrations for several pollutant mixtures at stratospheric conditions. Measurements of NO and $CFCl_3$ concentrations at altitudes of 20 to 30 kilometers, obtained from references 16 and 17, are listed in table II. These concentrations are 10^3 to 10^5 times smaller than the reaction chamber concentrations in our experiments. Also given in this table is the value of J_7, the O_2 photolysis rate constant used for each of the three altitudes listed. These J_7 values were taken from reference 18. For each altitude condition the reaction mechanism, without any wall destruction reactions, was used to compute O_3 concentration against time out to the steady-state condition. We assumed, for each altitude condition, that air containing the tabulated amounts of NO and $CFCl_3$ was irradiated until a steady-state O_3 concentration was reached. These steady-state O_3 concentrations are given in table II along with the corresponding O_3 concentration that was computed for the irradiation of pure air. The last column in this table shows the percentage of reduction in the pure-air O_3 concentration in the presence of the pollutants. Clearly, this computation shows a very large O_3 reduction at altitude conditions due to the presence of $CFCl_3$ and NO.

Figure 10 shows the results of computations that compare the effect of each pollutant separately with that of the combined mixture. The computations are for 25-kilometer-altitude conditions. Figure 10(a) shows results for the atmospheric NO and $CFCl_3$ concentrations given in table II. In this case, $CFCl_3$ alone gives the smallest reduction (20 percent) in the steady-state O_3 concentration. Nitric oxide alone gives about the same O_3 reduction (~50 percent) as the mixture of the two pollutants. Figure 10(b) shows the results of a similar computation, but with the pollutant concentrations both made 100 times the present measured values. These high concentrations could possibly be reached in the stratosphere if emissions continue unchecked. The

results now show a steady-state O_3 concentration reduction of more than 95 percent for all three pollutant mixtures. In this case, NO alone gives the smallest reduction, but the differences among the mixtures are rather trivial.

These computations do not give values for actual O_3 reduction in the stratosphere. The chemical model used is only one part of a complete atmospheric model. Indeed, the inclusion of transport phenomena in the computation does make the computed reductions of O_3 much smaller (e.g., ref. 19). The computations were performed to show that the chemical mechanism that explains O_3 destruction in our experiments also predicts O_3 destruction at stratospheric conditions.

DISCUSSION AND CONCLUDING REMARKS

In this work we have compared the effects of different pollutant mixtures on O_3 formation during the photolysis of air. In our laboratory experiments we have studied O_3 formation in the presence of small amounts of molecular chlorine (Cl_2) alone, small amounts of trichlorofluoromethane ($CFCl_3$) alone, and mixtures of these compounds with nitric oxide (NO). Apparent interaction between the NO_x and ClO_x destruction cycles for O_3 was observed. For Cl_2-NO mixture 1 (2-ppm Cl_2 and 2-ppm NO), O_3 destruction was more than for 2-ppm Cl_2 alone but only slightly less than for 2-ppm NO alone. For mixture 2 (4-ppm Cl_2 and 2-ppm NO) the situation was more complicated. At first, O_3 destruction was less than for either 4-ppm Cl_2 alone or 2-ppm NO alone. Ozone concentration rose but then reached a maximum value and decreased. The strikingly different behavior of these two Cl_2-NO mixtures is only partially explained by our reaction mechanism. For mixture 2, the computations show the observed O_3 maximum quite nicely. The O_3 peak occurs at the same time as a computed peak in the $ClONO_2$ concentration. This indicates that formation of $ClONO_2$ at first prevents O_3 destruction as it ties up both NO and the chlorine species. However, after about 60 minutes of reaction time, $ClONO_2$ starts to be destroyed, releasing ClO_x species, and O_3 destruction increases. For mixture 1, computations predict the same temporary tie-up of the ozone-destroying species by $ClONO_2$. However, this was not observed experimentally. There was no maximum in the O_3 concentration early in the reaction, only a very slight leveling off for a short time. It is not very likely that $ClONO_2$ would be more stable in this experiment than when the higher amount of Cl_2 is present. The discrepancy may be due to a combination of such factors as (1) an incomplete reaction mechanism and (2) additional surface effects.

The $CFCl_3$-NO mixture also temporarily stopped O_3 destruction, but at a later reaction time. The $CFCl_3$ alone, NO alone, and the mixture of both had about the same strong destructive effect on O_3 in air. The computations reproduced the O_3, NO, and

NO_2 profiles quite well for the one mixture studied, although this might not be the case for different mixtures of $CFCl_3$ and NO.

Our gas-phase chemical model indicates very little interaction between the ClO_x and NO_x reactions when applied to mixtures of NO and $CFCl_3$ at stratospheric conditions. Essentially no counteraction of O_3 destruction was observed for the individual pollutants. One purpose of these computations was to determine the ability of $ClONO_2$ formation to counteract O_3 destruction. The indication is that $ClONO_2$ is not a major sink for chlorine atoms at stratospheric conditions. This agrees with the computed results of reference 11.

In summary, we have shown that O_3 destruction by mixtures of Cl_2 or $CFCl_3$ with NO can be explained by a chemical mechanism involving the formation and destruction of $ClONO_2$. The mechanism explains the important results of these experiments. Computations indicate that $ClONO_2$ is not an important factor in preventing O_3 destruction either at the experimental conditions or at stratospheric conditions.

Lewis Research Center,
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TABLE I. - REACTIONS IN ClO_x-NO_x SYSTEM

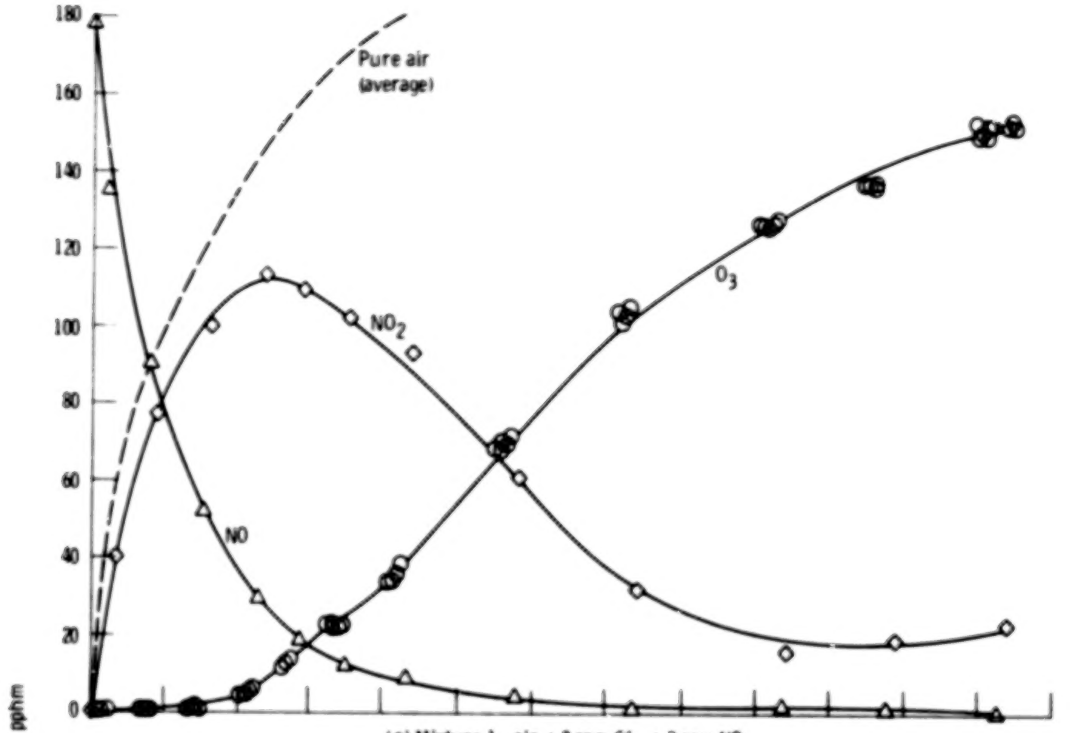
Number	Reaction	Coefficients in equation $k = AT^N \exp(-E_a/RT)$[a]				Reference
		A	N	E_a		
				J/mole	cal/mole	
I	$Cl + O_3 \rightarrow ClO + O_2$	1.3×10^{13}	0	1422	340	20
II	$O + ClO \rightarrow Cl + O_2$	3×10^{13}		0	0	21
III	$Cl_2 + h\nu \rightarrow 2\ Cl$	5.9×10^{-4}		0	0	1
IV	$2\ Cl + M \rightarrow Cl_2 + M$	5.8×10^{14}		-6694	-1600	22
V	$ClO + h\nu \rightarrow Cl + O$	2×10^{-3}		0	0	22
VI	$O + Cl_2 \rightarrow ClO + Cl$	5.6×10^{12}		12970	3100	23
VII	$O_2 + h\nu \rightarrow O + O$	See text				
VIII	$O_3 + h\nu \rightarrow O + O_2$	3.55×10^{-3}		0	0	1
IX	$O + O_2 + M \rightarrow O_3 + M$	3.8×10^{13}		-4226	-1010	1
X	$O + O_3 \rightarrow O_2 + O_2$	1.1×10^{13}		19120	4570	1
XI	$2\ ClO \rightarrow ClO_2 + Cl$	2×10^{10}		0	0	[b]24
XII	$Cl + ClO_2 \rightarrow Cl_2 + O_2$	9.4×10^{13}		0	0	25
XIII	$ClO_2 + M \rightarrow Cl + O_2 + M$	7.8×10^{12}		8326	1990	22
XIV	$NO + O_3 \rightarrow NO_2 + O_2$	3.4×10^{11}		9979	2385	[b]26
XV	$O + NO_2 \rightarrow NO + O_2$	1×10^{13}		0	0	[b]26
XVI	$NO_2 + O_3 \rightarrow NO_3 + O_2$	8×10^{10}		20500	4900	27
XVII	$NO_2 + h\nu \rightarrow NO + O$	1×10^{-2}		0	0	[b]2
XVIII	$NO_3 + h\nu \rightarrow NO_2 + O$	1.3×10^{-2}				[b]26
XIX	$NO_2 + NO_3 + M \rightarrow N_2O_5 + M$	1×10^{18}				2
XX	$N_2O_5 + h\nu \rightarrow NO_2 + NO_3$	7.7×10^{-5}				2
XXI	$NO + ClO \rightarrow Cl + NO_2$	6.8×10^{12}		-1661	-397	28
XXII	$ClO + NO_2 + M \rightarrow ClONO_2 + M$	1.6×10^{15}		-9037	-2160	29
XXIII	$ClONO_2 + h\nu \rightarrow ClO + NO_2$	4.3×10^{-4}		0	0	10
XXIV	$O + ClONO_2 \rightarrow ClO + NO_3$	2×10^{12}		6987	1670	12
XXV	$Cl + ClONO_2 \rightarrow Cl_2 + NO_3$	1×10^{12}		5063	1210	30

[a]k has units of sec^{-1} for photochemical reaction, cm^3/mole sec for bimolecular reaction, and $cm^6/mole^2$ sec for termolecular reaction. R = 8.3143 J/mole K (1.98717 cal/mole K).

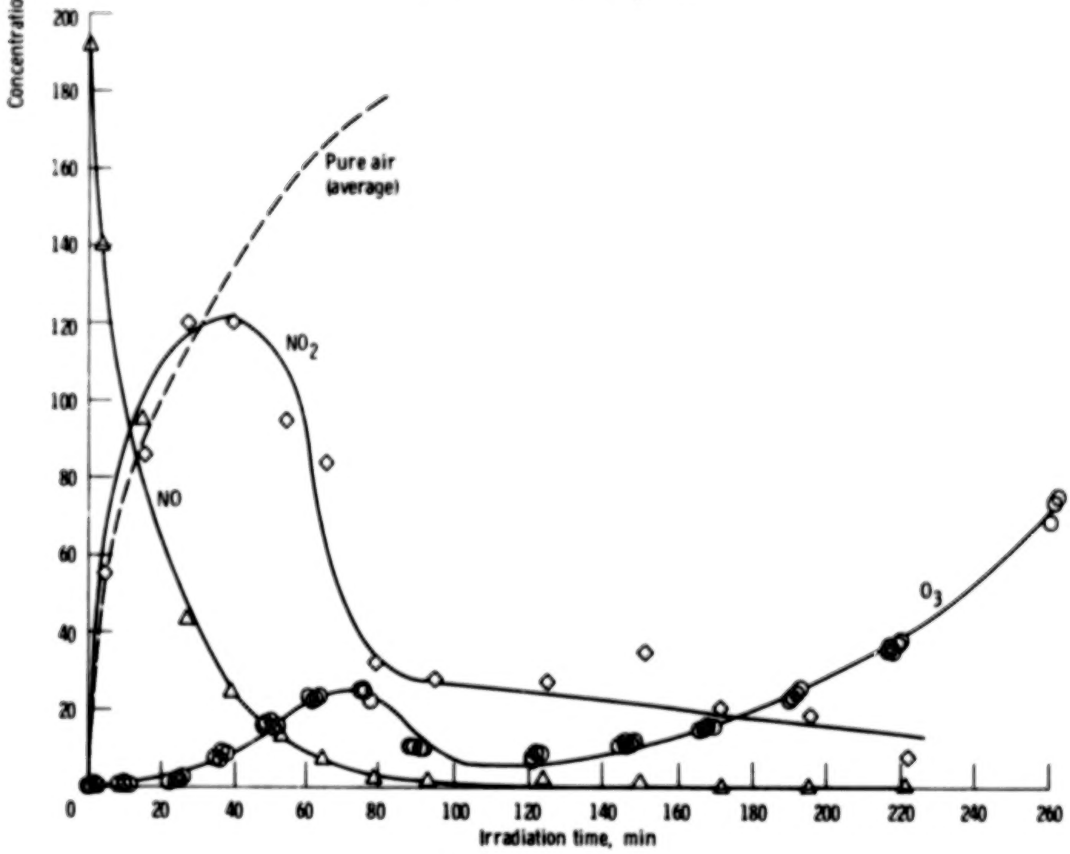
[b]Value adjusted from value given in reference.

TABLE II. - COMPUTED O_3 DEPLETION BY NO AND $CFCl_3$ IN AIR AT STRATOSPHERIC CONDITIONS

Altitude, km	$CFCl_3$ concentration, parts per trillion	NO concentration, parts per billion	Rate constant, J_7, sec^{-1}	O_3 concentration in pure air, ppm	O_3 concentration with pollutants, ppm	Reduction in O_3, percent
20	50	0.27	1×10^{-13}	2.35	0.55	77
25	18	.8	1.3×10^{-12}	4.90	2.36	52
30	9	2.6	1×10^{-11}	8.02	3.81	52



(a) Mixture 1: air + 2 ppm Cl_2 + 2 ppm NO.



(b) Mixture 2: air + 4 ppm Cl_2 + 2 ppm NO.

Figure 1. - Concentration-time profiles for NO, NO_2, and O_3 in air-Cl_2-NO mixtures.

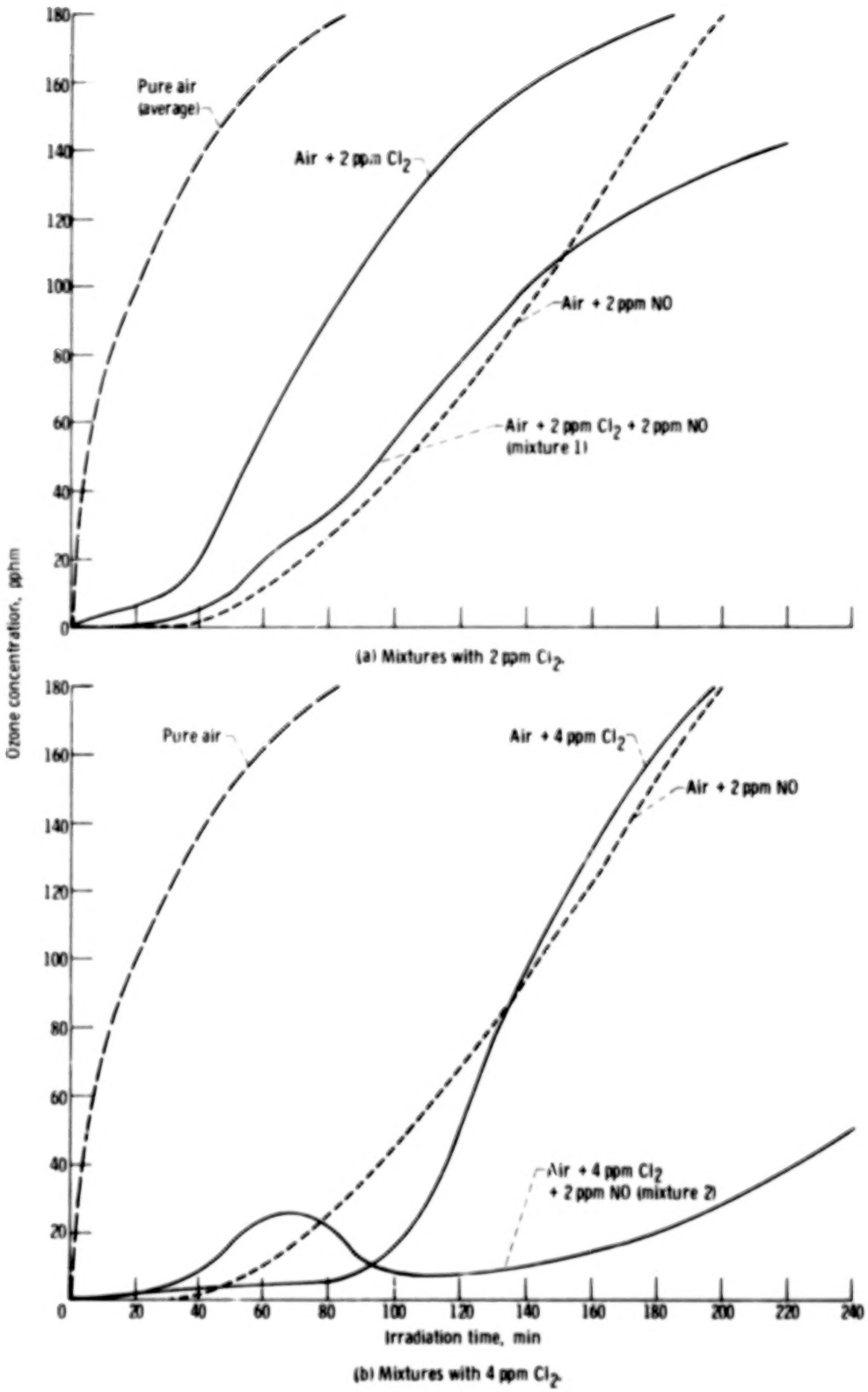

Ozone concentration, pphm
Pure air (average)
Air + 2 ppm Cl_2
Air + 2 ppm NO
Air + 2 ppm Cl_2 + 2 ppm NO (mixture 1)
(a) Mixtures with 2 ppm Cl_2.
Pure air
Air + 4 ppm Cl_2
Air + 2 ppm NO
Air + 4 ppm Cl_2 + 2 ppm NO (mixture 2)
Irradiation time, min
(b) Mixtures with 4 ppm Cl_2.

Figure 2. - Ozone formation in air-Cl_2 and air-Cl_2-NO mixtures.

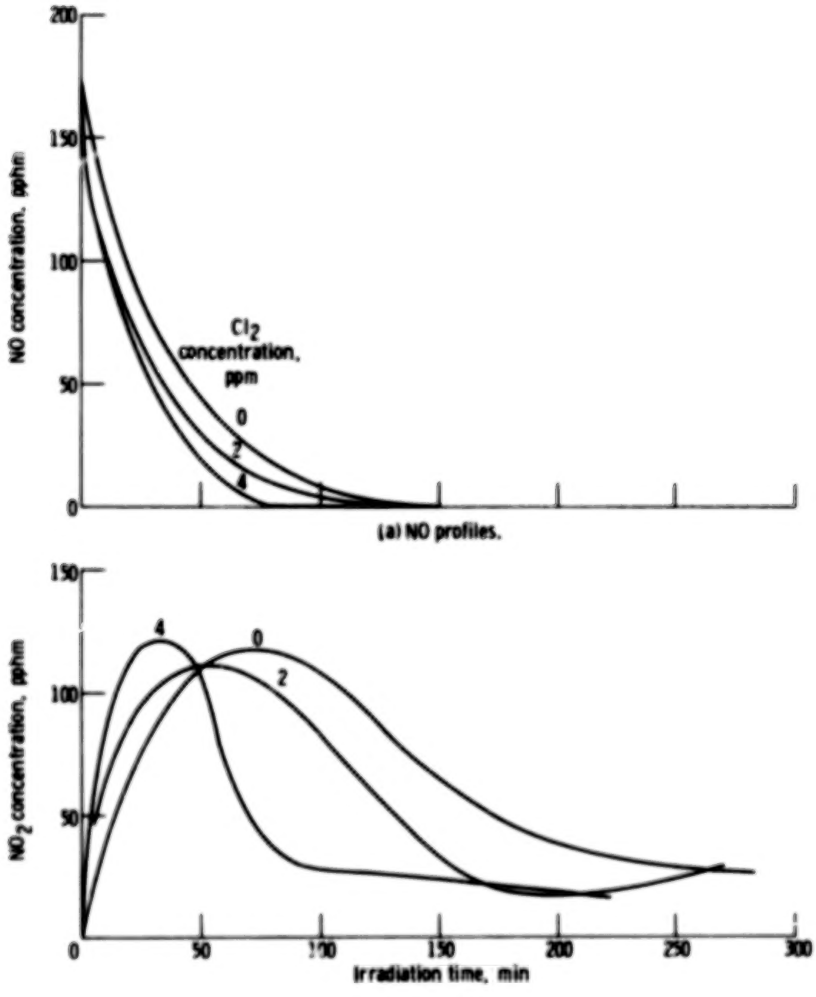


Figure 3. - Effect of adding Cl_2 on conversion of NO to NO_2 and consumption of NO_2. Nitric oxide initial concentration, 1.8 ppm.

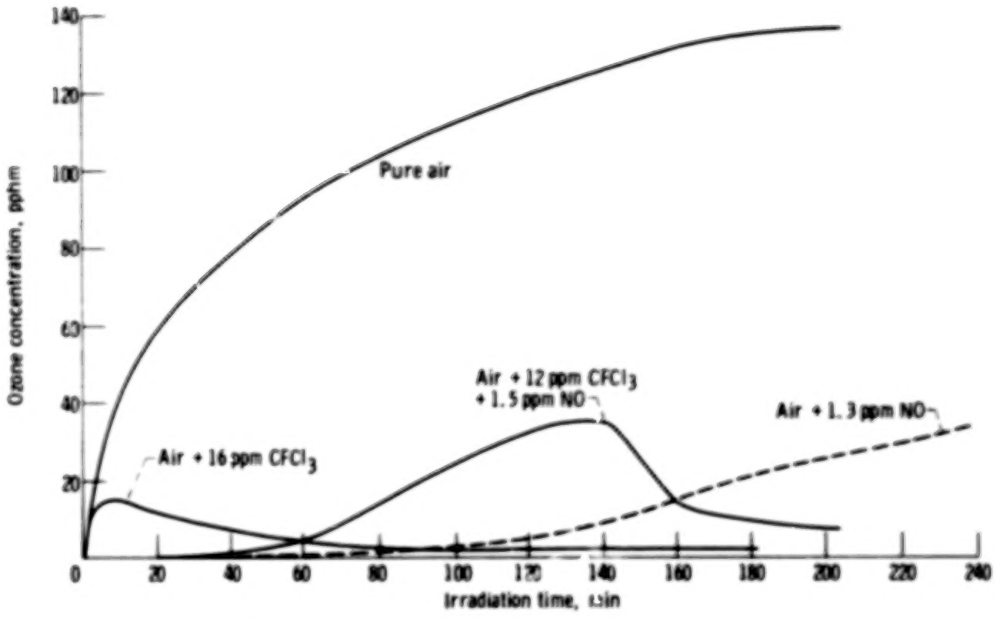


Figure 4. - Formation of O_3 in air-$CFCl_3$ and air-$CFCl_3$-NO mixtures.

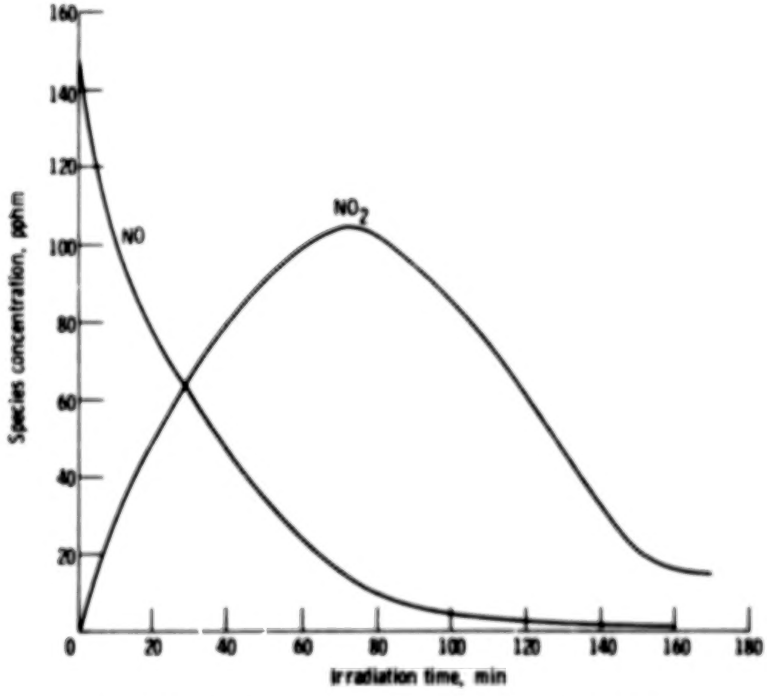
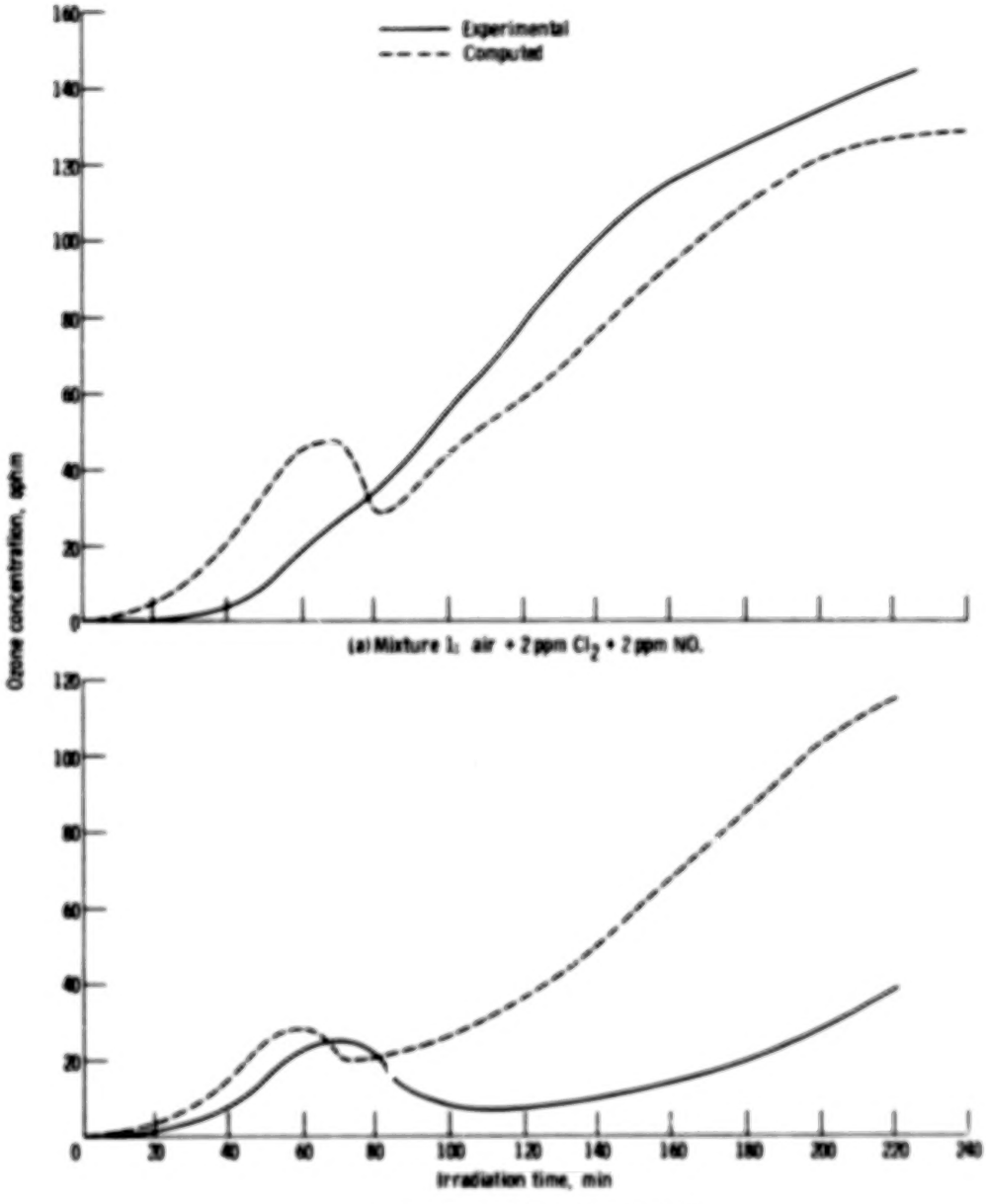


Figure 5. - Formation of NO and NO_2 in air + 12 ppm $CFCl_3$ + 1.5 ppm NO.



(a) Mixture 1: air + 2 ppm Cl_2 + 2 ppm NO.

(b) Mixture 2: air + 4 ppm Cl_2 + 2 ppm NO.

Figure 6. - Comparison of experimental and computed ozone formation in air-Cl_2-NO mixtures.

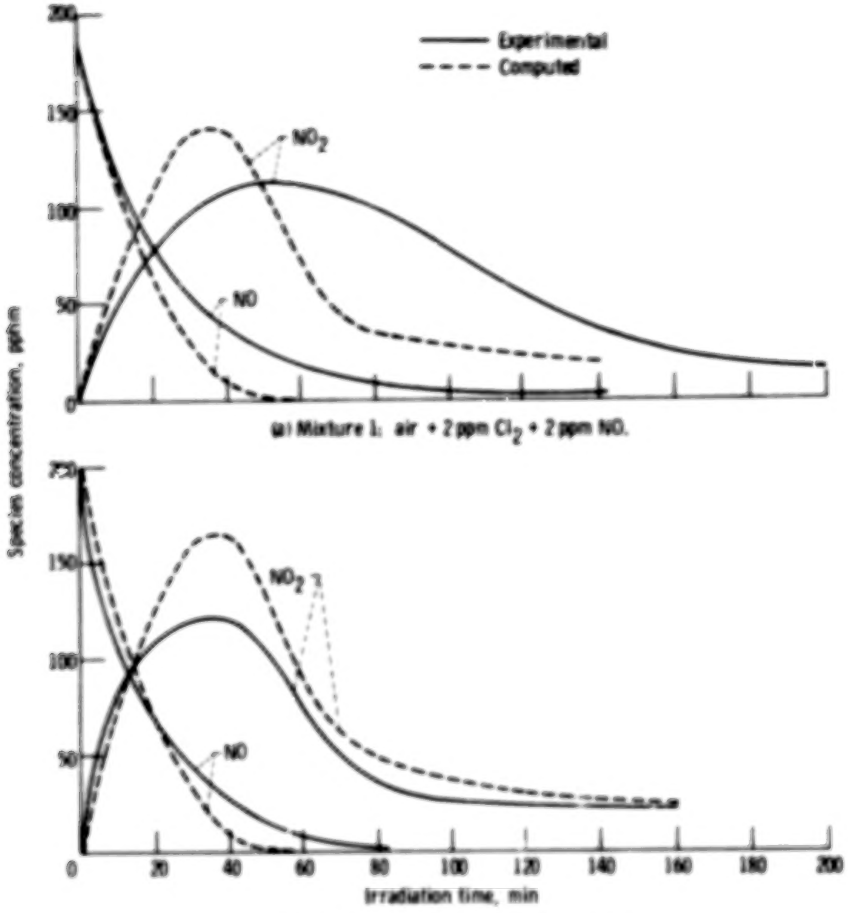


Figure 7. - Comparison of experimental and computed NO and NO_2 formation in air-Cl_2-NO mixtures.

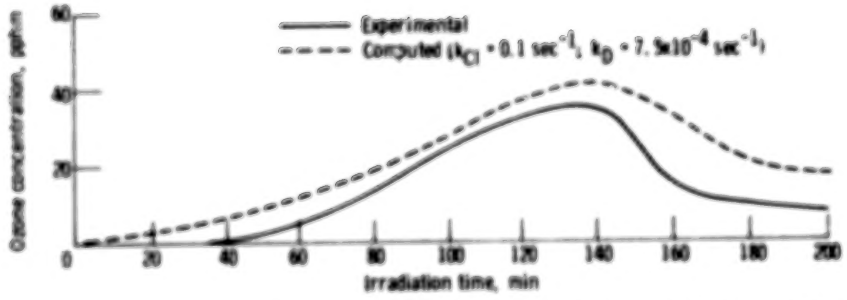


Figure 8. - Comparison of experimental and computed O_3 formation for air + 12 ppm $CFCl_3$ + 1.5 ppm NO.

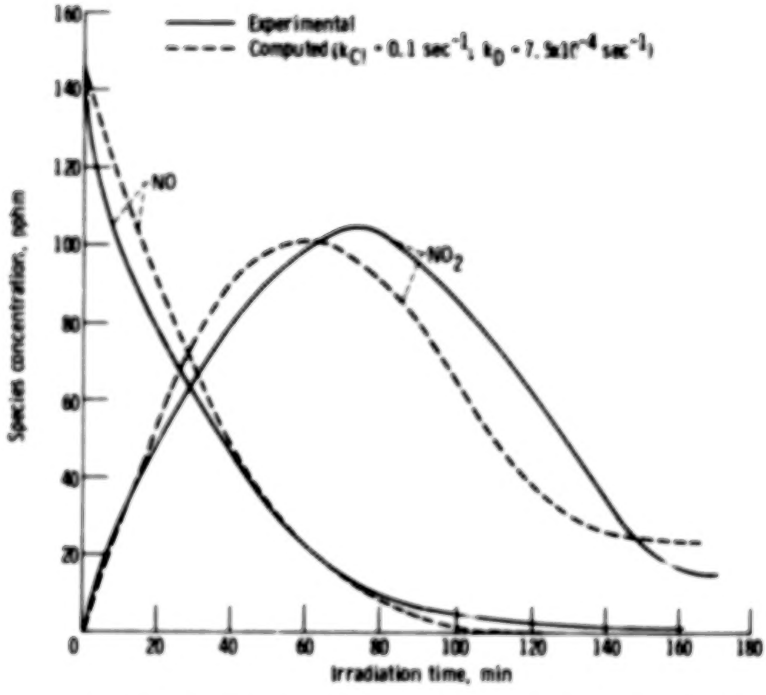
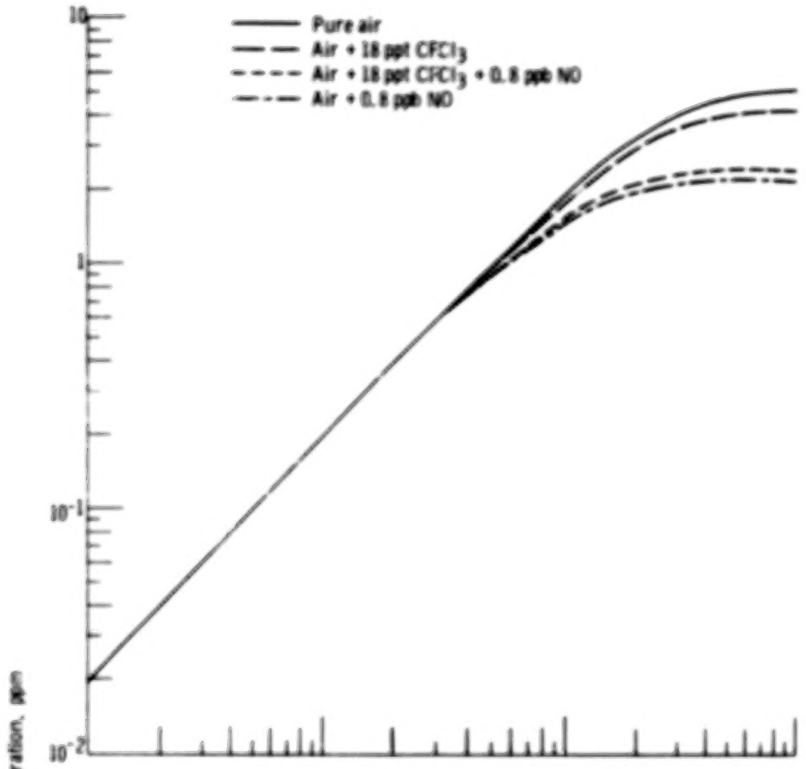
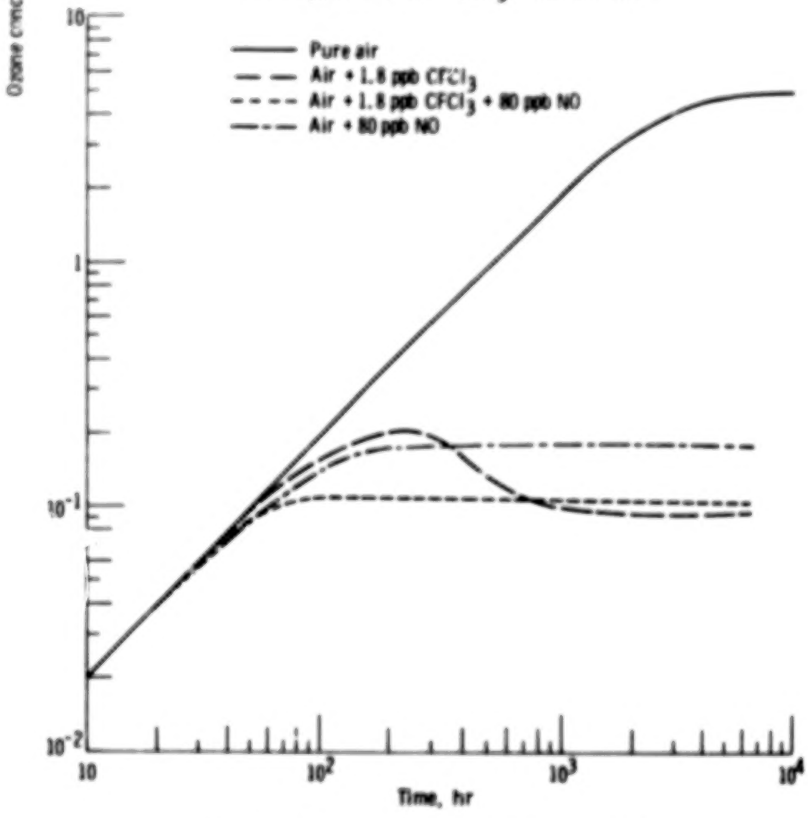


Figure 9. - Comparison of experimental and computed NO and NO_2 formation for air + 12 ppm $CFCl_3$ + 1.5 ppm NO.



(a) Using present NO and $CFCl_3$ concentrations.



Ozone concentration, ppm

(b) Using 100 times present NO and $CFCl_3$ concentrations.

Figure 10. - Computed O_3 formation at 25-kilometer-altitude conditions (temperature, 222 K; pressure, 0.0252 atmosphere).

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16 Abstract

Ozone formation in a reaction chamber at room temperature and atmospheric pressure has been studied for the photolysis of mixtures of NO with either Cl_2 or $CFCl_3$ in air. Both Cl_2 + NO and $CFCl_3$ + NO in air strongly inhibited O_3 formation during the entire 3- to 4-hour reaction. A chemical mechanism that explains the results is presented. An important part of this mechanism is the formation and destruction of chlorine nitrate ($ClONO_2$). Computations were performed with this same mechanism for $CFCl_3$-NO-air mixtures at stratospheric temperatures, pressures, and concentrations. Results show large reductions in steady-state O_3 concentrations in these mixtures as compared with pure air. This work shows that $ClONO_2$ is not a significant sink for the O_3-destroying Cl atoms. It was not a major factor in preventing O_3 destruction in the laboratory experiments and probably will not be in the stratosphere either.

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